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(57) Abstract

Dinitrosyl ferrohemochrome encapsulated in a film of edible polymer is used in a nitrite-free meat-curing process, to confer on the cured-meat product colour characteristics of nitrite-cured meats. The encapsulated DNFH is protected against oxidative degradation to enhance its shelf life, and is readily dispersible in aqueous pickle solutions. The encapsulating polymer is suitably an edible polysaccharide such as beta-cyclodextrin, preferably in admixture with other edible polysaccharides. The meat-curing system of the present invention additionally includes an antioxidant and an antimicrobial agent. Comminuted meat products such as sausage meats and wieners are made by simply mixing in an appropriate amount of the encapsulated pigment as part of the curing process prior to further processing. Solid meat products such as hams are made by injecting or pumping into them pickle solution in which the encapsulated pigment has been dispersed.

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NITRITE-FREE MEAT CURATIVE AND PROCESS OF CURING MEAT

TECHNICAL FIELD

This invention relates to meat curing components and processes for their use, and more particularly to compositions and methods for the replacement of sodium nitrite in the curing of meat. More specifically, it relates to the application of a preformed cooked cured-meat pigment, dinitrosyl ferrohemochrome (DNFH), along with other ingredients of a nitrite-free meat-curing system such as an antioxidant and an antimicrobial agent. DNFH is the component of an alternative curing system which is responsible for the pink colour characteristic of nitrite-cured meats.

BACKGROUND ART

Current meat-curing practice, which is founded upon the ancient art of preserving meat with salt, employs the addition of nitrite (and in certain products, nitrate) along with salt, sugar, various reducing agents, and phosphates to meat.

The role of nitrite in cured meat is three-fold: i) it provides the characteristic pink-red cured-meat colour to the lean tissue; ii) it inhibits the outgrowth of a number of food poisoning and spoilage bacteria; and iii) it contributes to the distinct flavour of cured meat and retards the development of oxidative rancidity (or warmed-over flavour). Of these functions, the second one is considered the most vital. In this regard, it is considered that the most important role of nitrite is to prevent the outgrowth of and toxin formation by Clostridium botulinum. The distinct colour and flavour are nevertheless integral parts of a cured-meat product.

Despite these beneficial effects on cured-meat products, there is concern about the use of nitrite as a food additive. This derives from the fact that N-nitrosamines (e.g., N-nitrosopyrrolidine and N-nitrosodimethylamine) are formed, albeit in the parts-per-billion range, by the reaction of nitrite with amines or amino acids which are present in food, and such N-nitrosamines are carcinogenic. In addition, the existence of residual nitrite in cured meat increases the body's total nitrite load, and this in turn may lead to an increased likelihood of nitrosamine formation within the human stomach.

Due to the potential health hazard associated with the use of sodium nitrite, there has been extensive study to find methods to eliminate it from meat-curing practice. It is, however, desirable to retain the characteristic colour of cured meat, ordinarily developed by the reaction of nitrite with the natural meat pigment myoglobin, to form dinitrosyl ferrochrome (DNFH). The role of colour in the perception of overall quality is very significant.

United States Patent 4,559,234 Rubin et al., issued December 17, 1985, describes and claims a nitrite-free composition for curing meats, which comprises dinitrosyl ferrohemochrome, an antioxidant, a sequestering agent, and an antimicrobial agent. Curing of meats with the preferred embodiments of the compositions described in this patent produces an essentially nitrite-free meat product, indistinguishable in colour and flavour from nitrite cured meat. This patent describes the antioxidative properties of the combination of DNFH with various antioxidants, chelators and antimicrobial agents.

DNFH is obtainable synthetically from the hemin prepared from the hemoglobin in beef blood, by reaction with nitric oxide in the presence of a reducing agent. This is described by Shahidi et al., J. Food Sci., 50:272, 1985. However, DNFH is very susceptible to light-induced oxidation and subsequent fading. Even when stored in the dark

in oxygen-free conditions, its shelf life is not greater than about four to five weeks.

Moreover, DNFH is a fine crystalline solid which is sparingly soluble in either water or curing brine. Consequently, it is a difficult material to handle. It is difficult to achieve a uniform distribution of DNFH within an intact cut of meat, because it is so slightly soluble in injectable aqueous solutions. These factors provide technical drawbacks to the system and processes described in the aforementioned patent of Rubin et al.

There has been a number of reports in the prior art of attempts to provide nitrite-free meat- curing systems, whilst retaining a pink colouration of the final product which imitates that imparted by DNFH. These include:

Sebranek, Food Technol 33(6):58, 1979 who reports the testing of various natural pigments, of which beet pigment seemed the most promising.

Dymicky et al., J. Food Sci. 40:306, 1975 and Grossblatt (ed) "Alternatives to the Current Use of Nitrite in Foods", National Academy Press, 1982, who report studies of over three hundred compounds for their ability to form pink hemochromes in meat, without finding a satisfactory nitrite replacement.

Other reports of attempts to provide nitrite-free meat-curing systems include the following:

Gray and Pearson, Advances in Food Res., 29:1, 1984 reported that a number of constituents, including potassium sorbate, sodium hypophosphite, methyl and ethyl esters of fumaric acid, and lactic acid-producing bacteria have proven to be effective anti-microbial agents.

Wood et al., J. Food Protect 49:691, 1986 suggests that sodium hypophosphite is the best potential nitrite substitute, particularly

in a nitrite-free meat-curing composition which contains dinitrosyl ferrohemochrome.

U.S. Patent 4,798,729 Anders et al. shows that sodium lactate presents a possible alternative to the use of nitrite as an anti-botulinal agent.

European Patent 0 122 062 B1 Dahlstrom, assigned to Stauffer Chemical Co., teaches that the incorporation of from 25 - 50 ppm of the compound 3-(4-tolylsulfonyl) acrylonitrile into meat effectively inhibits the outgrowth of C. botulinum.

DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a novel, nitrite-free curing system for meat products utilizing a pigment of improved stability and dispersibility.

It is a further object of the invention to provide a novel process for curing meats which avoids the use of nitrites whilst retaining substantially equivalent colour properties in cured meat as obtained by nitrite curing, utilizing such a pigment.

It is a further object of the invention to provide a means for achieving dispersal of pigment into solid meat cuts.

From one aspect, the present invention provides encapsulated particles of the cooked, cured-meat pigment dinitrosyl ferrohemochrome (DNFH), the particles being encapsulated within a wall of edible, film-forming polymer. These encapsulated particles according to the invention are stabilized against light-induced oxidation, to the extent that their shelf life is increased several fold over that of the unencapsulated DNFH. Moreover, they are readily dispersible in aqueous fluids such as pickle solutions. Accordingly, not only are the encapsulated DNFH particles of the invention useful in conferring colour on comminuted meat products such as sausage meat, but they can also

be used to colour solid cuts of meat such as ham, in an even, uniform manner.

From another aspect, the present invention also provides a process for curing meat products, which comprises adding to the meat product, either a comminuted meat product or a solid, intact meat product, microencapsulated dinitrosyl ferrohemochrome particles, along with other curing ingredients, and appropriately cooking the meat products.

BEST MODE FOR CARRYING OUT THE INVENTION

Curing systems according to the invention also include additionally at least one antioxidant and at least one antimicrobial agent. These may be provided at least partially within the microcapsules along with the DNFH, as part of the microcapsule walls, or as separate ingredients.

The encapsulating process for preparing the microcapsules of DNFH may be conducted by many of the encapsulation processes known in the art, but particularly preferred is a spray-drying process. In this process, a dispersion of DNFH particles in a solution of the film-forming polymer in an appropriate solvent, e.g. water, is prepared. This dispersion is then fed to a spray dryer, and atomized therein using a non-oxygen containing gas, and microencapsulated product is recovered from the spray dryer. Preferably also, the DNFH particle size is reduced, prior to the encapsulation process, to a very fine crystalline solid e.g. by homogenization. The particle size of DNFH prior to encapsulation should be as small as possible, and as uniform as possible, if the pigment is to be injected into solid meat cuts. In practice, particle sizes of up to about 8 microns are acceptable, but preferred are particle sizes of about 2 microns or less.

The encapsulating material is preferably a natural film-forming polymer, most preferably a polysaccharide or carbohydrate. Specific examples of preferred materials include beta-cyclodextrin, maltodextrin, N-Lok * (a commercial modified starch, manufactured by National Starch and Chemical Corp., Bridgewater, N.J.) and gum arabic (or gum acacia). The pigment appropriately constitutes from 0.5 - 5% by weight, preferably from about 1 - 3% by weight, of the microcapsules ("payload").

Compositions according to the invention also include at least one antioxidant. Suitable anti-oxidants are those commonly used in food systems and include ascorbic acid, physiologically acceptable salts of ascorbic acid such as sodium ascorbate, ascorbyl palmitate, erythorbic acid, ascorbyl acetal, butylated hydroxy anisole (BHA), butylated hydroxytoluene (BHT), t-butylhydroquinone (TBHQ), dl-alpha-tocopherol, propyl gallate, nordihydroguaiaretic acid, lecithin, dilauryl thiodipropionate, and natural antioxidants such as deflavourized rosemary spice extract. The amount of antioxidant, present as part of the microcapsules, is from about 0.1 - 1 part antioxidant per part of DNFH, preferably from 0.25 - 0.75 per part. A second quantity of antioxidant is used, along with the pickle, in greater amount.

Preferred compositions of the curing system according to the invention also include a sequestering agent, for the purpose of enhancing lipid stability. Suitable sequestering agents include monosodium phosphate, disodium phosphate, sodium hexametaphosphate, sodium tripolyphosphate, sodium pyrophosphate, sodium citrate, citric acid, monoglyceride citrate, 8-hydroxyquinoline, sodium gluconate, catechol, ethylenediamine tetraacetic acid, disodium ethylenediamine tetracetate, diethylenetriamine penta-acetic acid and salicylic acid. Certain of these sequestering agents, e.g. sodium EDTA, can in fact contribute to the oxidative stability of the compositions of this

invention. They may be provided as separate ingredients. Suitable amounts are from about 10 milligrams - 1,000 milligrams per kg of non-phosphate, and from about 1,000 milligrams to 6,000 milligrams per kg of phosphate-containing sequestering agent, based on the weight of the cured meat produced.

The composition of the curing system of the present invention also includes an antimicrobial agent. Suitable antimicrobial agents include sodium hypophosphite, potassium sorbate, lactic acid-producing bacteria, sodium lactate, 3-(4-tolyl sulfonyl) acrylonitrile, nisin, propylparahydroxybenzoate, methyl fumarate, and dimethyl fumarate; ethyl fumarate and diethyl fumarate. Generally, suitable amounts of antimicrobial agent range from about 50-5,000 milligrams per kilogram of cured meat product. Optimum amounts are dependent on the choice of antimicrobial agent. For example, sodium lactate may be used at levels of up to 4%.

A particularly preferred embodiment of the invention is microcapsules which include dinitrosyl ferrohemochrome, encapsulated in a combination wall material comprising beta-cyclodextrin and one of maltodextrin, N-Lok, or gum arabic, along with sodium ascorbate and ascorbyl palmitate.

In preparing the compositions of the preferred embodiments of the present invention, for spray drying to effect encapsulation, all of the ingredients may be prepared as an aqueous dispersion. The pigment DNFH should be reduced in particle size to the aforementioned very fine particle form. Then the dispersion is fed to the spray dryer. Suitably, the solids content of the dispersion, i.e. the DNFH in the solution of wall material and other ingredients, is from about 5.0 to 20% for best results, dependent to some extent upon the design of the spray dryer being used.

The encapsulated pigment of the present invention is employed as a component of a nitrite-free meat-curing composition. A satisfactory pink colour in the meat is achieved with the addition of about 10 - 60 milligrams of DNFH per kilogram of meat and meat additives. The amount of encapsulated pigment required is calculated on the basis of the capsule payload and the total weight of the cured-meat products (before cooking).

In respect of nitrite-free comminuted meat product such as wieners, the encapsulated pigment is easily applied in the production process. The composition of pigment, antioxidant, antimicrobial and, optionally, sequestering agent, which can be supplied as a preformed mixture or kit in appropriate size and proportions, merely needs to be thoroughly mixed into the meat emulsion, and oxygen excluded from the meat emulsion. Alternatively, the emulsion could be prepared in standard equipment, then transferred to a vacuum mixer, the air removed therefrom and then the encapsulated pigment is added and mixed into the emulsion under substantially oxygen-free conditions. The resultant meat product, after processing, is substantially identical in taste and appearance to a similarly prepared nitrite-cured product. In respect of wieners, the DNFH provides a more than adequate pink colour provided that the amount of beef in the wiener mixture is not excessive. When a high proportion of beef or other strongly coloured meat, i.e. a meat with a relatively high myoglobin content, is being used, the colour contribution of the preformed pigment can be hidden or be obscured by the natural brown pigments of the cooked meat. This is because, unlike nitrite, DNFH is primarily a colour additive, and does not convert the native pigment, myoglobin, into the cooked cured pigment as in the case of nitrite. Instead, DNFH adds colour to a background colour of the cooked uncured meat, and so it must mask or hide this background colour in order to provide a pink colour to the final cooked product. In

respect of light-coloured meats such as chicken, turkey, pork or fish, this does not constitute a problem. An ideal pink colour can be imparted to them by use of this encapsulated DNFH, so that the product is ideally suited for use with wieners or sausage products composed mainly of light coloured meats such as chicken, turkey, pork or fish. The encapsulated DNFH of the present invention can also be used in dark meat mixtures, such as mixtures of beef and mutton, with light coloured meats, provided that the light coloured meat is present in major proportion.

According to another aspect of the invention, however, the encapsulated DNFH pigment is also applied to solid cuts of meat so as to prepare, for example, nitrite-free hams, picnics, cottage rolls and bacon. It can also be used to prepare cured poultry products of a similar nature. To effect this, the encapsulated pigment is first dispersed in a pickle solution, which, by way of example, may contain appropriate levels of the following ingredients such that their concentrations in the meat (based on wet weight of meat and meat additives) are: about 2% salt; about 1% sugar; about 0.3% phosphate sequestering agent; about 0.06% sodium ascorbate and/or other appropriate antioxidant; and an appropriate amount of antimicrobial agent. An amount of pickle solution ranging from about 10 - 50% of the meat's initial weight is injected by pumping into the meat.

Prior to conducting this injection step, the DNFH/pickle dispersion should preferably be treated under oxygen-free conditions with some means of particle size reduction or deagglomeration. This is a separate and distinct particle size reduction step from that conducted prior to the encapsulation process by spray drying. This deagglomeration procedure when using an injectable pickle solution is performed to counteract the tendency of the DNFH microcapsules to combine to form clumps or agglomerates upon introduction of the

encapsulated pigment into the pickle solution. Following this deagglomeration step, the dispersion is preferably immediately injected into the meat, for example using a multiple injection technique. Injection needles with multiple outlet ports provided in their side walls and directed radially away from the needle stem can be used, in conjunction with suitable pumps. By such techniques, one can obtain total perfusion of the meat product, with substantially even distribution of the encapsulated DNFH pigment throughout the solid meat, to give a substantially uniform colour to the meat product as a whole.

Prior to injecting the solid meat cut with the pigment dispersion, it is advantageous to subject the meat cut to a tumbling or massaging process, eg. for 2-4 hours continuously. This has the apparent effect of rendering the muscle fibre sheathes within the meat less resistant to penetration by the pigment dispersion. Atmospheric pressure or vacuum tumbling can be used for this purpose.

Following the injection of the dispersion into the solid meat, the meat is then physically treated by tumbling or massaging, to assist in the dispersion of the pigment evenly throughout the meat. This, for example, may take place in a rotary drum tumbler for a substantial period of time, e.g. intermittently over a 9 - 18 hour period, at a rotational speed of, for example, 10 - 15 rpm. Atmospheric pressure or vacuum tumbling can be adopted. After tumbling, the meat is conventionally treated, to cook and package it.

In this manner, an essentially nitrite-free product, with a uniform pink colour which is virtually indistinguishable from that of a nitrite-cured product, is obtained.

The invention is further described, for illustrative purposes only, in the following specific examples.

REAGENTS AND EQUIPMENT

All the chemicals used in these examples were reagent or food-grade materials, unless otherwise specified, and were used without any further purification. The cooked cured-meat pigment, dinitrosyl ferrohemochrome, was prepared from hemin and nitric oxide, in buffered solutions, as reported by Shahidi et al. (Can. Inst. Food Sci. Technol. J., 17(1):33, 1984; J. Food Sci., 50:272, 1985).

The spray dryer was a Büchi 190 model, with co-current flow and a pneumatic nozzle atomizer. The tumbler consisted of a rotary stainless steel drum, with lucite baffles.

GENERAL PROCEDURE FOR MICROENCAPSULATION OF PIGMENT

As microencapsulation by spray drying consists of emulsification (or dispersion) and dehydration, it was first necessary to prepare a fine dispersion of the pigment in a solution of the encapsulating agent(s). Thus, the feed material to the spray dryer was a dispersion in which the continuous phase was the dissolved wall material and the disperse phase was the dinitrosyl ferrohemochrome.

An appropriate amount of encapsulating agent was weighed, keeping in mind the desired capsule payload and solids content of the feed. The wall material consisted of the following ingredients or combinations of ingredients: 10 - 100% beta-cyclodextrin, and 0 - 90% maltodextrin or 0 - 90% N-Lok or 0 - 20% gum arabic. In addition, sodium ascorbate or ascorbic acid were added, as antioxidants, in an amount such that the weight-to-weight ratio of ascorbate to dinitrosyl ferrohemochrome was between 0.25 and 0.75. The antioxidant and wall material were dissolved in distilled water to form the continuous phase of the feed dispersion. A small amount (about 0.5ml per 100ml) of 50%

(w/w) sodium hydroxide was added to aid in the dissolution of the beta-cyclodextrin.

In the meantime, the dinitrosyl ferrohemochrome was separated from the buffered solution in which it was prepared (either by centrifugation or other means), and then dispersed in a small quantity (25-50 ml) of distilled water. This dispersion was then treated, under nitrogen, with a Polytron Homogenizer (Brinkman Instruments, Model PT 10/35, PTA-20S generator) for 2 min at an instrument setting of '6' (about 10,000 rpm). The purpose of this process was to reduce the average size of the pigment particles. This "homogenized" DNFH (disperse phase) was added to the aforementioned solution of wall material (continuous phase) and the entire feed dispersion was further treated with the Polytron (setting of '5', about 1 min) to ensure feed homogeneity prior to spray drying.

The spray dryer was equipped with a pneumatic nozzle atomizer. Nitrogen was used as the atomizing gas in order to minimize the exposure of DNFH to oxygen. Nitrogen pressures between 25 and 50 psig (170 kPa and 350 kPa) were used. Table 1 shows the range of spray-dryer operating conditions that were used. The quality of the encapsulated pigment was not overly dependent on the operating parameters of this particular spray dryer.

TABLE 1

SPRAY DRYER OPERATING CONDITIONS

Parameter	Levels
inlet air temp.	120 - 165°C
feed flow rate	4-7 ml/min
nitrogen pressure	20-50 psig (170-350 kPa)

The feed container was wrapped in aluminum foil to

minimize light exposure, and kept under nitrogen to minimize contact with oxygen. The dispersion was fed to the spray dryer via a peristaltic pump at a rate between 4 and 7 ml/min. The dried DNFH microcapsules were collected in a cyclone and stored in sealed glass sample bottles, in the dark.

With the spray dryer that was used, typical recoveries of encapsulated pigment were between 75 and 85% (based upon the weight of solids in the feed dispersion). Encapsulated samples with nominal payloads of 2%(i.e., 0.250g DNFH/12.5g of encapsulating agent) had measured payload values between 2.2 and 2.6% largely due to certain aspects of the spray-drying process. Some of the carbohydrate wall material was selectively lost during spray drying, resulting in capsule payloads which were slightly higher than expected. Inspection of the encapsulated DNFH under a scanning electron microscope revealed the majority of particles to be spherical, with a diameter between 5 and 12 microns. The spheres were, for the most part, smooth with some slight surface wrinkling.

The encapsulated products were judged according to their ability to provide a pink colour to ground pork as compared to a 150 ppm sodium nitrite control. The standard pigment-testing procedure involved initially weighing 40 g of lean ground pork into a 150 ml beaker. Calculated portions of spray-dried pigment (usually 10 - 60 ppm of DNFH) were dispersed in 10 ml of distilled water. This dispersion was then added to the ground pork and a glass rod was used to mix the pigment thoroughly into the pork. The meat sample was cooked in a constant temperature bath for approximately 40 min at 85°C. The colour of the cooked sample was then judged against that of the nitrite control. The samples of encapsulated pigment were studied over time and some were found to be stable for over 1 year (as compared to 4-6

h for an aqueous dispersion of non-encapsulated DNFH which was exposed to both light and air).

The encapsulated pigment, once prepared, may be used as the colour component of a nitrite-free meat-curing composition, or as simply a colour additive to enhance the appearance of traditionally-cured (i.e. nitrite-cured) or uncured meats.

GENERAL PROCEDURE FOR PRODUCTION OF NITRITE-FREE CURED MEATS USING ENCAPSULATED DINITROSYL FERROHEMOCHROME

For comminuted meats, the incorporation of encapsulated dinitrosyl ferrohemochrome was simple. For wieners, appropriate levels of various meats (i.e., pork, beef, mutton, chicken, turkey or fish, etc.) and meat additives (i.e., water/ice,salt, sugar, phosphate sequestering agent(s), antimicrobial agent(s), antioxidant(s) binders and spices) were weighed in accordance with the desired formulation. The beef level should be carefully controlled because of its tendency to obscure the colour contribution of the DNFH. The formulation was cut into a fine paste in a manner which minimizes oxygen contact with the pigment, eg. using a vertical cutter/mixer with a vacuum attachment, or a vacuum cutter. The encapsulated DNFH was added to the vertical cutter/mixer after the water/ice and just prior to all of the other wiener ingredients. The meat/fat was the last item added to the cutter so that splattering of the ingredients was minimized. A vacuum of approximately 28" Hg was used throughout the cutting step. From here, the meat emulsion was stuffed into wiener casings and cooked/smoked in a controlled humidity smokehouse until an internal temperature of 65-75°C was reached. It is evident that the preformed pigment can be readily applied with relatively few changes to the standard wiener-producing operations.

For the solid-cuts applications, meat cuts (e.g., for hams, the inside, outside, and round) were obtained by the manual deboning of whole hams. Individual whole muscles were used for each experimental run in order to remove the inherent variability that using meat cuts composed of different muscle groups would present.

The aqueous curing pickle was prepared on the basis of a 20-30% gain in the fresh weight of the meat. The concentrations of the various ingredients in the pickle were such as to produce the following levels in the final cured product (before cooking): salt, about 2%; sucrose, about 1%; ascorbate, about 0.06%; phosphate-containing sequestering agent (usually STPP), about 0.3%; an appropriate amount of antimicrobial agent (e.g., in the case of sodium hypophoshite, about 0.3%); and dinitrosyl ferrohemochrome, 30-40ppm (mg/kg). Some phosphates eg. STPP and sodium hexametaphosphate also improve the water binding capacity of the meat.

The preformed cooked cured-meat pigment, dinitrosyl ferrohemochrome, was combined with the rest of the curing brine immediately before injection into the meat. So that the DNFH should be well-dispersed in the injection solution, the entire DNFH/pickle mixture was treated with the Polytron homogenizer prior to injection. This facilitated the movement of the DNFH within the muscle tissue by decreasing the average particle size of the pigment. The treatment consisted of 1-2 min of homogenization, under nitrogen, at an instrument setting of '6' (about 10,000 rpm). Another means of particle-size reduction could be substituted. If desired, a particle classification could be used to ensure that only DNFH particles below a certain diameter (i.e., particles as small as possible but with a maximum diameter of 1-2 microns) are injected into the meat cut and the rest are recycled/re-processed. In all of this processing, the presence of oxygen and light should be minimized.

The resultant "homogenized" pickle dispersion was injected into the meat tissue. A multiple-injection technique was used to ensure that each section of the cut received an equal volume of pickle. The injection needle was made with a series of holes along its length to allow pickle to radiate outwards from the entire length of the needle and not just downwards from the tip. The needle was small enough to allow for a great many injection sites in each cut. The sites were spaced evenly at a distance of 1-2 cm. This injection procedure enables one to "induce" a uniformity of pigment by distributing the pickle injection sites around the cut of meat. This effectively minimizes the distance the DNFH has to move in order to achieve a uniform distribution or decreases the diffusion distance. Multiple-injection machines consisting of an array of needles, similar in design to the needle used in these experiments, are available in present-day meat-curing practice.

After injection, the meat is physically treated in order to accelerate the curing process and to hasten the movement of the pigment. This is accomplished by a process of tumbling or massaging, techniques known in the art. Vacuum tumbling and vacuum massaging can also be used, and commercial equipment to do this is available. In the present case, it was carried out in a rotating drum. The duration of the tumbling was usually 9 h although some cuts were tumbled for as long as 18 h. Normally, the ratio of tumbling time to relaxation time was 15 min to 45 min, but on/off ratios as high as 15 min/15 min were tested. The rotational speed of the tumbler was 10-15 rpm. Tumbling time refers to the time period during which the drum was rotating and the meat was being physically treated. Relaxation time refers to the period when tumbling was halted to allow the pickle ingredients to diffuse through the cut and to allow the meat to re-absorb its own juices.

It was postulated that intra-muscular collagen (i.e., the collagen sheaths surrounding individual muscle fibres and bundles of

fibres; referred to as the endomysium and the perimysium, respectively) provided the major resistance to pigment movement within the muscle. A 3 h (continuous) tumbling treatment of the fresh meat, prior to pickle injection, was found to alleviate this interference to some extent.

After the physical processing, the cured meat sample was wrapped in an impermeable plastic film, or vacuum packaged, and stored in the refrigerator for two days, prior to cooking. The meat was then cooked in a water bath (at 75 - 80°C) to an internal temperature of 65 - 70 °C. Lastly, the meat was sliced (in many directions) and inspected for colour uniformity and quality, and sensory testing.

EXAMPLE 1

MICROENCAPSULATION OF SYNTHETIC DINITROSYL FERROHEMOCHROME

For the preparation of DNFH microcapsules with a wall material of 100% beta-cyclodextrin, 12.50 g beta-cyclodextrin and 0.15g sodium ascorbate were weighed into a 150 ml beaker. Using a glass rod, this powder was mixed into a fine paste with the addition of 10-15 ml distilled water. More water was added to bring the total volume to approximately 50 ml. Care was taken to ensure that no clumps existed in the resultant cloudy-white suspension. At this point 10-20 drops of 50% (w/w) sodium hydroxide were added to dissolve the encapsulating agent. The mixture was stirred with a magnetic stirrer until a clear (slightly yellowish) solution of the encapsulating agent was produced.

The synthetic DNFH was present as a suspension of 125 mg of pigment in 125 ml of buffer solution in a 250-ml polyethylene centrifuge tube. The pigment was separated from the buffer by centrifuging for 10 min at 4000 rpm. Two such tubes, i.e., 250 mg DNFH, were used for the preparation of one batch of microcapsules (with a nominal payload of 2%). The pigment (from both tubes) was

dispersed in approximately 50 ml of distilled water. This suspension was then treated, under nitrogen, with the Polytron Homogenizer for 2 min at an instrument setting of '6' (about 10,000 rpm). This step was taken to minimize the size of the DNFH particles and improve feed homogeneity.

The DNFH was then mixed with the solution of wall material. This whole feed dispersion was diluted to 125 ml (with distilled water) and treated mildly (1 min @ '5') with the Polytron before spray drying. The nominal payload of the DNFH microcapsules was 2% (0.250g DNFH/12.5g encapsulating agent) and the feed solids content was around 10% (12.5g solid in 125ml). The feed dispersion was spray dried with the operating conditions listed in Table 1.

The dried microcapsules were collected, weighed and stored in sealed glass sample bottles (in the dark). Tests on ground pork showed that pigment coated with beta-cyclodextrin imparted a pink colour which was virtually indistinguishable from that provided by nitrite. Furthermore, some of these encapsulated samples were stable for at least one year.

EXAMPLE 2

ALTERNATIVE ENCAPSULATING AGENTS

Dinitrosyl ferrohemochrome was encapsulated in a combination of gum arabic and beta-cyclodextrin using the procedure of Example 1. Encapsulating agents consisting of 80-90% beta-cyclodextrin and 10-20% gum arabic were particularly good. For the preparation of DNFH microcapsules coated in 85% beta-cyclodextrin and 15% gum arabic, 10.625 g beta-cyclodextrin and 1.875 g gum arabic were used and the procedure of Example 1 was followed. The pigment preparations encapsulated with this wall material were of the

highest quality in terms of both their stability and the colour they provided to ground pork.

EXAMPLE 3

ALTERNATIVE ENCAPSULATING AGENTS

An encapsulating agent of 70% N-Lok, 20% beta-cyclodextrin, and 10% gum arabic produced good results. The colour such an encapsulated product imparted to ground pork was an acceptable pink although it was not quite as bright as the colour provided by nitrite. These samples were prepared by combining 8.75 g N-Lok, 2.50 g beta-cyclodextrin, and 1.25 g gum arabic, and following the procedure of Example 1 to encapsulate 0.25 g of dinitrosyl ferrohemochrome. This encapsulating medium greatly decreases the amount of expensive beta-cyclodextrin necessary.

EXAMPLE 4

ALTERNATIVE ENCAPSULATING AGENTS

A similar combination to the one in Example 3, with the major component being maltodextrin, of dextrose equivalent D.E = 4.0, also yielded good-quality encapsulated DNFH. The wall material consisted of 80% maltodextrin, 15% beta-cyclodextrin, and 5% gum arabic. Encapsulated pigments with a payload of 2% were prepared as in Example 1. These products were found to impart a colour to ground pork much like the colour provided by the samples in Example 3.

EXAMPLE 5

ALTERNATIVE ENCAPSULATING AGENTS

It was found that the modified starches maltodextrin and N-Lok were able substitutes for the gum arabic which was included in the encapsulating media of Examples 2 - 4. For instance, a product with a

coating of 20% beta-cyclodextrin and 80% maltodextrin (D.E.=25.0) was prepared by combining 2.50g beta-cyclodextrin with 10.0g maltodextrin, and following the procedure of Example 1. The colour provided to ground pork was very attractive indeed; it was identical in appearance to that of a nitrite-treated product. A particle investigation, using scanning electron microscopy, revealed that DNFH microcapsules coated in the above wall material were particularly smooth and free of surface imperfections.

EXAMPLE 6

ALTERNATIVE ENCAPSULATING AGENTS

A product equivalent to the one in Example 5, except with N-Lok instead of maltodextrin, was prepared according to the procedure of Example 1. This coating of 20% beta-cyclodextrin and 80% N-Lok served to protect the pigment and preserve its ability to impart a pink colour to ground pork. In fact, the colour, like that produced by the encapsulated pigment of Example 5, was indistinguishable from that of the nitrite control sample. Thus, either maltodextrin or N-Lok can be combined with beta-cyclodextrin to produce a very good encapsulating medium for dinitrosyl ferrohemochrome. There is no noticeable difference between the two (i.e. maltodextrin D.E.=25 and N-Lok) regarding their effect as components of the protective wall material.

EXAMPLE 7

ENCAPSULATING MEDIA WHICH DO NOT CONTAIN BETA-CYCLODEXTRIN

Pigment was coated in either maltodextrin (D.E.=25.0) or N-Lok alone. These materials offered the advantages of complete water solubility (i.e., no NaOH required) and ready availability. The colour provided by pigment products encapsulated in either maltodextrin or N-

lok alone was inferior to that obtained when beta-cyclodextrin was used as a wall component, as was the quality and stability of the microcapsules. They are nevertheless useful materials. However, a minimum of 10% beta-cyclodextrin should preferably be present.

EXAMPLE 8

RANGE OF INGREDIENTS IN ENCAPSULATING MEDIUM

The pigment-encapsulating procedure was quite flexible with regard to the proportions of the various encapsulating agents within the overall capsule wall material. Tests were conducted over the whole range of combinations of beta-cyclodextrin and maltodextrin (or N-Lok). Good encapsulated products were prepared with encapsulating agent combinations of 10-90% beta-cyclodextrin and corresponding levels of 90-10% maltodextrin (or N-Lok). For instance, encapsulated pigments prepared with a wall material of 10% beta-cyclodextrin and 90% maltodextrin (or N-Lok) provided ground pork with a proper pink colour. Pigment preparations coated in a 50/50 mix of beta-cyclodextrin and maltodextrin (or N-Lok), or in 90% beta-cyclodextrin and 10% maltodextrin (or N-Lok) yielded excellent results as well. The colour imparted to ground pork consistently ranked between 9 and 10 on a scale of 10 (where nitrite=10). Hence, it was evident that a wide range of combinations of beta-cyclodextrin with maltodextrin or N-Lok could be used to achieve exceptional results. This broad range of acceptable combinations means that the DNFH-encapsulating medium may be optimized on the basis of cost considerations.

EXAMPLE 9

APPLICATION OF ENCAPSULATED DINITROSYL FERROHEMOCHROME TO A COMMINUTED MEAT PRODUCT CONSISTING ENTIRELY OF PORK

A series of trials was conducted in order to test the feasibility of using DNFH in comminuted meat products. Pilot-plant-scale sausage-making equipment was used. For each trial, one experimental (DNFH) run was performed along with one control (nitrite) run. Also, t-butyl hydroquinone (TBHQ), and sodium hypophosphite (NaH_2PO_2) were added to the nitrite-free wieners but not to the control batch.

In order to produce all-pork wieners, the required quantities of lean pork, backfat, and meat additives were weighed. The wiener formulation is shown in Table 2. The necessary quantity of encapsulated DNFH (to provide a 35 ppm level in the wieners prior to cooking/smoking) was weighed and dispersed in a known amount of water.

A specialized piece of evacuated equipment was used to prepare the wiener emulsion, namely a Stephan VCM-12 vertical cutter/mixer, with a vacuum attachment. The necessary amount of water/ice was placed in the VCM-12, followed by the DNFH and the other ingredients. Ice is preferable to water because the cutting action of the rotating blade is more effective at low emulsion temperatures. The meat (pork) and fat were placed on top of the water and powdered ingredients to help prevent the powder from splattering onto the walls of the bowl during cutting. A vacuum pump was used in order to evacuate the cutting chamber. It was left on throughout the cutting/mixing step. A vacuum of approximately 28" Hg (6 kPa) was achieved. A 3.5-minute processing time at a blade speed of 3500 rpm was used to prepare the emulsion.

The resultant wiener emulsion was stuffed out into a wiener casing using a piston stuffer. At this point, the wieners were placed into a controlled humidity smokehouse where they were cooked to a suitable internal temperature (65-75 °C).

It was found that the experimental (DNFH) wieners were identical in appearance to the nitrite-cured wieners. Both had good pink internal colours. The intensity of the pink colour given to the experimental wieners was readily controllable by a simple adjustment of the DNFH concentration. However, the pink colour in the nitrite-cured wieners is wholly dependent on the level of native myoglobin present in the meat block and is thus not readily adjustable. Organoleptic evaluations showed that nitrite-free wieners prepared using DNFH were no less acceptable, from a flavour standpoint, than those prepared with nitrite.

TABLE 2

PURE-PORK WIENER FORMULATION

Constituent	DNFH Run (g)	Control Run (g)
Lean Pork (80/20)	2267	2267
Pork Backfat	400	400
Ice	930	930
Binder	283	283
Salt	90	78.7
Seasoning	24	24
STPP	12.0	12.0
Sodium Ascorbate	2.1	2.1
Prague Powder (6.4% $NaNO_2$)	--	12.5
DNFH (encapsulated)	7.0	--
Na-hypophosphite	12.0	--
TBHQ	0.13	--

EXAMPLE 10

APPLICATION OF ENCAPSULATED DINITROSYL

FERROHEMOCHROME TO A COMMINUTED MEAT PRODUCT CONSISTING OF PORK AND BEEF

Wieners consisting of a meat block which was 75% pork, 10% beef, and 15% pork backfat, were prepared in the same manner and using the same non-meat formulation as in Example 9. The meat formulation was 2,000g lean pork, 400g pork backfat and 267 g of lean beef (80/15). Because of the presence of the beef, 45 ppm of synthetic pigment were used for the nitrite-free wieners. The higher pigment level was deemed necessary to compensate for whatever effect the beef would have in masking the colour contribution of the DNFH. In addition, a higher concentration of synthetic pigment is required just to mimic the colour of the nitrite control. This control batch is more strongly coloured than corresponding all-pork controls because of the greater myoglobin content, due to the presence of beef in the emulsion. The wieners were satisfactory in every respect, and in fact more beef could be tolerated, eg. up to 30%.

EXAMPLE 11

APPLICATION OF ENCAPSULATED DINITROSYL FERROHEMOCHROME TO A COMMINUTED MEAT PRODUCT CONSISTING ENTIRELY OF CHICKEN

Chicken wieners were prepared by the method of Example 9 and using exactly the same formulation as in Example 9 except that the meat component was 1867 g deboned chicken and 800 g of chicken thighs (i.e. no fat added). For the experimental (DNFH) wieners, a pigment level of 35 ppm was used.

The resultant wieners were surprisingly dark pink in colour

(i.e., both DNFH-treated and nitrite control). This was likely due to a high level of hemoglobin in the mechanically deboned meat. However, both sets were very similar in colour and were, in fact, virtually indistinguishable from each other. Therefore, DNFH may be successfully applied to chicken wieners as well as the more traditional pork/beef wieners.

EXAMPLE 12

PRODUCTION OF A NITRITE-FREE HAM USING ENCAPSULATED DINITROSYL FERROHEMOCHROME

For a meat cut weighing 1 kg, 300 g of a pickle solution or brine was used. As mentioned earlier, such a solution contains salt, sugar, sodium ascorbate, sodium tripolyphosphate, and sodium hypophosphite. If an encapsulated pigment with a 2% payload was used, one would require 2.275 g (i.e., $100/2.0 \times 35 \times 10^{-6} \times 1300g$) of encapsulated pigment to yield a level of 35 ppm DNFH, based on the total wet weight of the meat plus pickle.

The pigment was dispersed in the pickle solution with the aid of a glass rod. This pickle/DNFH dispersion was then homogenized with the Polytron for 1-2 min at a setting of '6' (about 10,000 rpm). This operation not only homogenized the pickle ingredients but reduced the average particle size of the pigment. It was found that pigment dispersions which had been treated had pigment particle (not encapsulated) diameters in the range of 1-5 microns while untreated dispersions consisted of particles mainly in the 7-20 micron range. This particle-size reduction step significantly improves the transport (or diffusion) properties of DNFH within solid cuts of meat. This, in turn, resulted in nitrite-free hams of more uniform colour. The cut of fresh ham had previously been subjected to a pre-injection tumbling treatment of 3 h (continuous) at 12 rpm. Such a treatment

rendered the ham more conducive to the movement of DNFH. At this point, the homogenized DNFH/pickle solution was injected into the ham using a manual multiple-injection technique. The needle used was a hypodermic needle which had a series of orifices drilled along its length to provide for a more random, radial flow pattern of pickle within the ham. The injection sites were placed at a distance of 1-2 cm from each other in order to ensure a complete and thorough coverage of the meat surface.

After injection, the meat sample was tumbled, in a rotary drum apparatus for 9 h @ 12 rpm with an on/off ratio of 15 min/45min. The cured meat was then sealed in an impermeable plastic film, and stored for two days in the refrigerator prior to cooking. A water bath @ 80°C was used to cook the ham to an internal temperature between 65 and 70°C. The resultant ham was judged to be virtually identical to a nitrite-cured ham in terms of colour, texture, flavour, and overall acceptability.

EXAMPLE 13

MODIFIED PROCEDURE FOR PREPARING NITRITE-FREE HAMS

In order to investigate the importance of DNFH particle size relative to the colour uniformity within the nitrite-free ham, the procedure of Example 12 was modified slightly. After the pickle/DNFH dispersion was homogenized with the Polytron, it was further subjected to a centrifuge treatment (i.e., 1-4 min @ 1000 - 3000 rpm). The intent of this additional step was to remove the larger DNFH particles, now presumably free of wall material, from the injection solution and thus, produce a more uniform pink colour within the ham. The results showed that the colour was indeed more uniform with no areas of high DNFH concentration.

What is claimed is:

1. Dinitrosyl ferrohemochrome particles encapsulated in an edible polymer film.

2. Encapsulated particles according to claim 1, wherein the polymer film is a polysaccharide film.

3. Encapsulated particles according to claim 2 wherein the particles have a size less than about 8 microns.

4. Encapsulated particles according to claim 2 wherein the particles have a size less than about 2 microns.

5. Encapsulated particles according to claim 2 wherein the polysaccharide is selected from the group consisting of beta-cyclodextrin, maltodextrin, N-Lok, gum arabic and mixtures of two or more of said polysaccharides.

6. Encapsulated particles according to claim 5 wherein the dinitrosyl ferrohemochrome constitutes approximately 0.5 - 5% by weight of the microcapsules.

7. Encapsulated particles according to claim 6 further including an effective amount of an antioxidant as an additional component of the microcapsules.

8. Dinitrosyl ferrohemochrome particles having a size in the range from about 1 - 5 microns, and being encapsulated in a polymer film of edible polysaccharide to form microcapsules, the polymeric

portion thereof consisting essentially of a mixture of from 10-90% by weight of beta-cyclodextrin and from 90-10% by weight of either maltodextrin, N-Lok or gum arabic, the microcapsules further incorporating an effective amount of antioxidant, the dinitrosyl ferrohemochrome constituting from about 0.5 - 5% by weight of the encapsulated product.

9. A process for preparing dinitrosyl ferrohemochrome particles encapsulated in an edible polymer film as defined in claim 1, which comprises:

comminuting dinitrosyl ferrohemochrome to a particle size range of less than about 8 microns;

dispersing the comminuted particles in a solution of edible polymer in a biocompatible solvent;

spray drying the dispersion so formed under substantially oxygen-free atomization conditions;

and recovering dinitrosyl ferrohemochrome encapsulated in edible polymer film in which the dinitrosyl ferrohemochrome constitutes about 0.5 - 5 weight percent of the encapsulated particles.

10. The process of claim 9 wherein the solids content of the dispersion subjected to spray drying is from about 5.0% to 20%.

11. The process according to claim 10 wherein the biocompatible solvent is water.

12. The process of claim 11 wherein the spray drying is accomplished by atomization using nitrogen gas.

13. The process of claim 12 wherein the solution of edible polymer is an aqueous solution of an edible polysaccharide selected from the group consisting of beta-cyclodextrin, maltodextrin, N-Lok, gum arabic and mixtures of two or more of said polysaccharides.

14. A process for preparing nitrite-free cured, processed-meat products having colour characteristics resembling those of nitrite cured processed-meat products, which comprises:

adding to a meat product an effective amount of microcapsules of dinitrosyl ferrohemochrome pigment encapsulated in an edible polymer film of polysaccharide, an effective amount of antioxidant, and an effective amount of at least one antimicrobial agent;

distributing the pigment substantially evenly throughout the volume of the meat product;

and processing the meat product with the pigment distributed therein.

15. The process of claim 14 wherein the meat product is a comminuted meat emulsion.

16. The process of claim 15 wherein the distribution of the pigment takes place under substantially oxygen free conditions.

17. The process of claim 16 wherein the amount of dinitrosyl ferrohemochrome pigment added is from about 10 - 60 milligrams per kilogram of meat and meat additives.

18. A process for preparing nitrite-free cured, processed solid meat products having colour characteristics resembling those of nitrite-cured, processed solid meat products, which comprises:

preparing a dispersion of encapsulated dinitrosyl ferrohemochrome according to claim 1 in a pickle solution;

deagglomerating the pigment particles in the pickle solution;

injecting the pickle solution with deagglomerated pigment particles therein into a solid meat product;

distributing said pickle solution substantially evenly throughout the volume of the solid meat product;

physically treating the meat product by tumbling or massaging;

and processing the solid meat product with the pigment distributed therein.

19. The process of claim 17 further including a step of tumbling or massaging the solid meat product prior to injecting the pickle solution therein.

20. The process of claim 19 wherein the amount of dinitrosyl ferrochrome pigment added by injection is from about 10 - 60 milligrams per kilogram of meat.

21. The process of claim 20 wherein the pickle solution is an aqueous dispersion of salt, sugar, sequestering agent, antioxidant and antimicrobial agent.

22. The process of claim 21 wherein the amount of pickle solution injected is from about 10 - 50% by weight of the initial weight of the meat.

23. The process of claim 22 wherein the injection and distribution of the pickle solution is accomplished by pumping the pickle solution into needles injected at multiple locations in the body of meat, said needles having a plurality of radially directed outlets.

INTERNATIONAL SEARCH REPORT

PCT/CA 91/00303

International Application

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B01J2/30; B01J13/04; A23B4/023; A23B4/027
A23B4/20; B01J2/30

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	B01J ; B01J ; A23B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	DE,A,3 221 737 (ERNST,RUDOLF.) 15 December 1983	
A	FR,A,2 013 613 (CPC INTERNATIONAL INC.) 3 April 1970	
A	US,A,4 559 234 (LEON J. RUBIN ET AL.) 17 December 1985 cited in the application	

° Special categories of cited documents :[10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10 DECEMBER 1991	03. 01. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	PYFFEROEN K.

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ANNEX TO [redacted] INTERNATIONAL SEARCH REPO[redacted]
ON INTERNATIONAL PATENT APPLICATION NO. CA 9100303
SA 50461

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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